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Short communication

Effect of gas ambient and varying RF sputtering power for bandgap narrowing of mixed (ZnO:GaN) thin films for solar driven hydrogen production

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HIGHLIGHTS

- Mixed (ZnO:GaN) thin film for solar driven hydrogen production.
- The mixed (ZnO:GaN) thin films deposited under Ar gas ambient failed to reduce the bandgap.
- Whereas, (ZnO:GaN) thin films grown under mixed O_2 and N_2 gas ambient showed bandgap reduction.
- The bandgap of (ZnO:GaN) thin films was tuned by varying the RF power.
- Enhanced crystallinity and visible light absorption resulted in improved photoresponse

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ABSTRACT

The ZnO and mixed (ZnO:GaN) thin films are synthesized by (RF) magnetron sputtering in Ar and mixed O_2 and N_2 gas ambient at 100 °C, followed by post-annealing at 500 °C in ammonia for 4 h. The mixed (ZnO:GaN) thin films deposited under Ar gas ambient failed to reduce the bandgap, whereas (ZnO:GaN) thin films grown under mixed O_2 and N_2 gas ambient showed bandgap reduction. The (ZnO:GaN) films deposited under mixed O_2 and N_2 gas exhibited enhanced crystallinity, with shifting the optical absorption into the visible light regions. The bandgap reduction in mixed (ZnO:GaN) thin films is realized by varying the RF power. As a result, mixed (ZnO:GaN) films grown under mixed O_2 and N_2 showed higher photocurrents than the mixed (ZnO:GaN) thin films deposited under Ar gas ambient. Our results indicate that reduced bandgap with enhanced PEC response can be attained using the appropriate gas ambient and by varying the RF power using mixed (ZnO:GaN) films.

1. Introduction

Photoelectrochemical (PEC) systems based on transition metal oxides, such as TiO_2, and WO_3, have received extensive attention since the discovery of photo-induced decomposition of water on TiO_2 electrodes [1–9]. Recently, ZnO has also been suggested as a candidate material for photoelectrochemical (PEC) applications such as hydrogen production [5]. Since ZnO possesses similar or even better optical and electronic properties than TiO_2 [7], (which has received much PEC attention in the past), it is expected to result in good PEC performance. The drawback of PEC systems, using these metal oxides, is that they have large bandgaps and cannot efficiently absorb visible light, which is the major fraction of the solar spectrum. Therefore, reducing the bandgap of these metal oxides is a critical issue for improving PEC applications of these oxides. In recent years intensive study on bandgap reduction of these metal oxides has been carried out.

So far, impurity incorporation has been the main method to reduce the bandgap of TiO_2. It has been reported that N-, C-, and S-doping can successfully narrow the bandgap of TiO_2 and push the photoresponse in the long-wavelength region [2,10–12]. Although bandgap reduction of TiO_2 has been extensively studied, very limited research exists on bandgap narrowing of ZnO by impurity incorporation. Significant amounts of dopant can only be

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incorporated into ZnO and WO_3 at low temperatures [13–15]. However, films deposited at low temperatures usually exhibit very poor crystallinity, which is extremely detrimental to the PEC performance. This dilemma hinders the PEC performance of dopant incorporated ZnO and WO_3 films. A possible cause for the inferior crystallinity is due to the uncompensated charged doped atoms. This problem may be overcome by using a heterogeneous photocatalysts: for example, ZnO:GaN solid solution. Mixed ZnO and GaN with a wurtzite-type structure gives an oxynitride with a unique structure and composition. ZnO has been used in a large variety of applications. For example, its wide bandgap of 3.3 eV and large exciton binding energy make it a promising material for UV optoelectronic devices [16]. GaN is also a well-known material with a bandgap of about 3.4 eV and has been studied extensively as laser diodes and light-emitting diodes [17]. GaN as a photoelectrode has been confirmed to have potential to split water under UV illumination [18]. A photoelectrode prepared using mixed ZnO and GaN achieves water splitting under visible light illumination [19]. Maeda et al. [19] recently reported that GaN:ZnO solid solution is one of the effective methods of bandgap narrowing, which has led to improved photoresponse in the long-wavelength region. However, to date, synthesis and PEC properties of mixed ZnO and GaN (ZnO:GaN) thin films have scarcely been studied.

In this paper, we report on the synthesis of mixed (ZnO:GaN) thin films by reactive RF magnetron sputtering in Ar, and mixed O_2 and N_2 ambient respectively. We found that the gas ambient plays a major role in bandgap narrowing of mixed (ZnO:GaN) thin films. The ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient exhibit enhanced crystallinity with a reduced bandgap compared to mixed ZnO:GaN(Ar) thin films deposited in Ar ambient. As a result, mixed ZnO:GaN(N_2/O_2) thin films presented improved PEC response, compared to ZnO:GaN(Ar) films. Furthermore, we found that the bandgap narrowing in ZnO:GaN(N_2/O_2) films can be effectively controlled by varying the RF power.

2. Experimental

Two sets of mixed (ZnO:GaN) thin films were deposited using ZnO and GaN targets. One set of sample was deposited in Ar gas ambient, we refer this set of samples as ZnO:GaN(Ar). The second set of sample was deposited in mixed N_2 and O_2 gas ambient, and is referred as ZnO:GaN(N_2/O_2). All the thin films were grown using an edwards auto 306 reactive RF magnetron sputtering system (Edwards, NY, USA). F-doped SnO_2 (FTO, 20–23 Ω/□)-coated transparent glasses (Sigma–Aldrich, St. Louis, MO, USA) were used as substrates. The distance between the target and substrate was 8 cm. The base pressure was below 5×10^{-6} Torr, and the working pressure for all synthesis was 2×10^{-2} Torr. Prior to sputtering, a pre-sputtering process was performed for 30 min to eliminate any contaminants from the target. Sputtering was then conducted with fixing the RF power of 35 W for GaN target and varying the RF power of ZnO target from 100 W to 300 W at 100 °C for ZnO:GaN(Ar) & ZnO:GaN(N_2/O_2) thin films, respectively. Substrates were rotated at 30 RPM during deposition to enhance film uniformity. For comparison, ZnO film was deposited in pure Ar ambient. All samples were controlled to have similar film thickness of about 1000 nm as measured by stylus profilometry.

The structure of synthesized films was characterized by X-ray diffraction (XGEN-4000, SCINTAG Inc., MA, USA, operated with a Cu Kα radiation source at 45 kV and 37 mA). The UV–VIS absorption spectra of the samples were measured by an n&k analyzer 1280 (n&k Technology, Inc. CA, USA) to investigate optical properties.

Photoelectrochemical measurements were performed in a three-electrode cell with a flat quartz-glass window to facilitate illumination to the photoelectrode surface [20–22]. The sputter-deposited films were used as the working electrodes with an active surface area of about 0.25 cm^2. Pt mesh and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. A 0.5-M Na_2SO_4 aqueous solution with a pH of 6.8 was used as the electrolyte for the PEC measurements and scan rate was 5 mV s^{-1} in this experiment. The photoelectrochemical properties of the samples were measured using a fiber-optic illuminator (Cole–Parmer, IL, USA) (150-W tungsten-halogen lamp) with a UV/IR filter. The light intensity was measured by a photodiode power meter. The total light intensity with the UV/IR filter only was fixed at 125 mW cm^{-2}.

Because our films were deposited on conducting substrates, measurements of electrical property by the Hall Effect were not possible. Instead, the electrical properties were measured by Mott–Schottky plots, which were obtained by AC impedance measurements. AC impedance measurements were carried out with a Solartron 1255 frequency response analyzer (Solartron Analytical, IL, USA) using the above three-electrode cells. Measurements were performed under dark conditions with an AC amplitude of 10 mV and frequency of 5000 Hz were used for the measurements taken under dark condition and the AC impedances were measured in the potential range of −0.7 V to 1.25 V (vs. Ag/AgCl reference). The series capacitor–resistor circuit model was used for Mott–Schottky plots [23,24].

3. Results and discussion

Fig. 1 shows the X-ray diffraction curves of ZnO, and mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient. It is seen that the ZnO film exhibits poor crystallinity, due to the low-temperature sputtering process. The ZnO:GaN(Ar) films deposited at ZnO(100 W)GaN(35 W) showed reduced crystallinity compared to that of the ZnO film. As the RF power of ZnO is increased to 200 W, ZnO:GaN(Ar) film showed improved crystallinity. The highest crystallinity was observed for ZnO:GaN(Ar) film deposited at ZnO(300 W)GaN(35 W) RF power. Crystallite sizes were 21 nm, 10 nm, 18 nm, and 28 nm for the ZnO, 100 W, 200 W, and 300 W RF power of ZnO target for mixed (ZnO:GaN) thin films, respectively, which were estimated by applying the Debye–Scherrer equation to our XRD data.

Fig. 2 shows the optical absorption coefficients of the ZnO, and mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient. The direct electron transition from valence to conduction bands was assumed

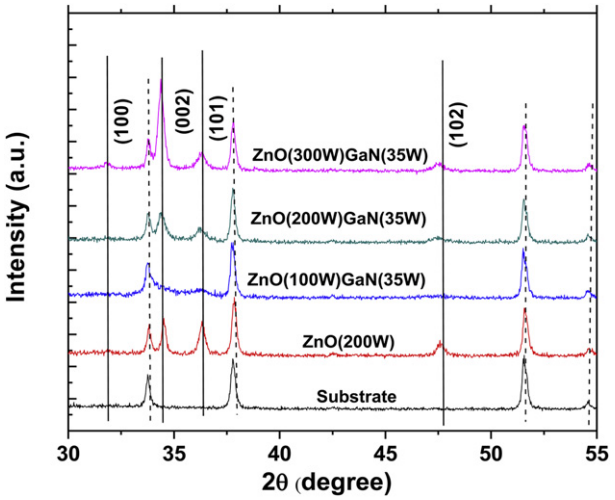

Fig. 1. The X-ray diffraction curves of ZnO, and mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient.

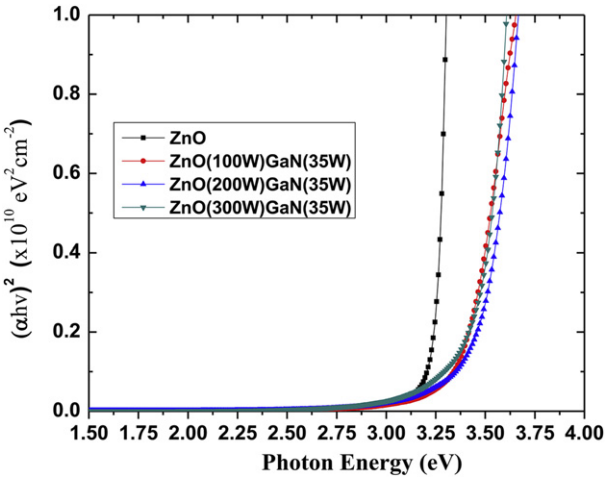

Fig. 2. The optical absorption coefficients of the ZnO, and mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient.

for the absorption coefficient curves, because ZnO and GaN films are known as direct-bandgap materials [25–27]. The optical bandgaps of the films were determined by extrapolating the linear portion of each curve. The bandgap of the ZnO film is 3.25 eV, which is consistent with the results reported elsewhere [28,13,14,20–22]. The direct optical bandgaps measured for mixed ZnO:GaN(Ar) thin films for 100 W, 200 W, and 300 W RF power of ZnO target are 3.52, 3.48, and 3.46 eV, respectively. It is clear that bandgap of mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient are failed to shift the optical absorption into the long wavelength region. Mott–Schottky plots of the ZnO and mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient (not shown here) exhibited positive slopes, indicating n-type semiconductors.

Fig. 3 shows the photocurrent–voltage curves of the ZnO and mixed ZnO:GaN(Ar) thin films, under illumination with the UV/IR filter. It showed clearly that the mixed ZnO:GaN(Ar) thin film deposited at ZnO(300 W)GaN(35 W) RF power showed the highest photocurrents, compared with any of the other films. The enhanced photocurrent may be due to the increased crystallinity of the film grown at ZnO(300 W)GaN(35 W) RF power. At a potential of 1.2 V, the photocurrents were 6.5, 7.9, 8.2, and 12.5 μA cm^{-2} for the ZnO, 100 W, 200 W, and 300 W RF power of ZnO for mixed ZnO:GaN(Ar) thin films, respectively. To investigate the photoresponses in the long-wavelength region, a green color filter (wavelength: 538.33 nm; FWHM: 77.478 nm) was used in combination with the UV/IR filter. The ZnO and mixed ZnO:GaN(Ar) thin films exhibited no clear photoresponse (not shown here), due to its wide bandgap nature. The modest photocurrents achieved in ZnO and mixed ZnO:GaN(Ar) thin film grown in Ar ambient are because its wide bandgap that limits absorption of UV light. Therefore, it is necessary to improve the crystallinity and reduce the bandgap of (ZnO:GaN) thin films, to make absorption in the visible region possible and use sunlight more efficiently. Using a correct ambient gas mixture in the chamber ambient may play significant role in improving the crystallinity and narrowing of bandgap for mixed (ZnO:GaN) thin films.

This is exactly the case for our second set of samples. Fig. 4 shows the X-ray diffraction curves of ZnO, and mixed ZnO:-GaN(N_2/O_2) thin films grown at fixed RF power of GaN target and varied RF power of ZnO target in mixed N_2 and O_2 gas ambient with N_2 mass flow rate of 75%. It is seen that the ZnO film exhibits poor crystallinity, may be due to the low-temperature combined with pure Ar gas ambient. The ZnO:GaN(N_2/O_2) films grown in mixed N_2 and O_2 gas ambient with N_2 mass flow rate of 75% show better crystallinity. The enhancement in crystallinity is attributed to the use of mixed N_2 and O_2 gas ambient. The (002), (100), and (101) peak is enhanced and (102) peak is decreased as the RF power of ZnO target is increased with the fixed RF power (35 W) of GaN target. Crystallite sizes were 21 nm, 18 nm, 34 nm, and 40 nm for the ZnO, 100 W, 200 W, and 300 W RF power of ZnO target for mixed (ZnO:GaN) thin films, respectively, which were estimated by applying the Debye–Scherrer equation to our XRD data.

Fig. 5 shows the optical absorption coefficients of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown at fixed RF power of GaN target and varied RF power of ZnO target in mixed N_2 and O_2 gas ambient with N_2 mass flow rate of 75%. The direct optical bandgaps measured for mixed ZnO:GaN(N_2/O_2) thin films at N_2 mass flow rate of 75% for increase in RF power of ZnO target, gradually decreased from 3.13 to 3.09 eV. It is shown theoretically that the bottom of the conduction band for (ZnO:GaN) is mainly composed of 4s and 4p orbitals of Ga, while N2p orbitals followed by Zn3d orbitals situated on the top of the valence band. The presence of Zn3d and N2p electrons in the upper valence band provides p–d repulsion for the valence band maximum, which results in

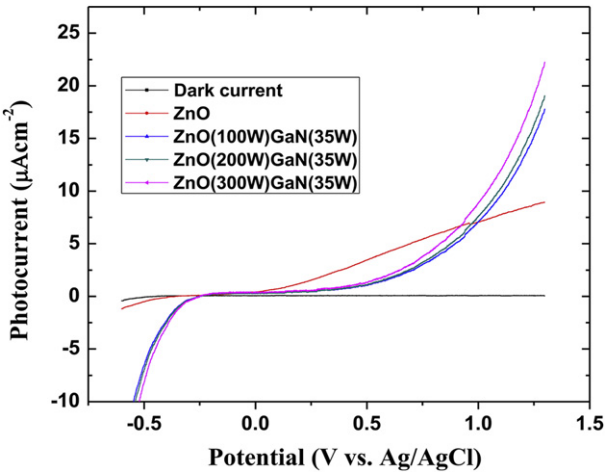

Fig. 3. Photocurrent–voltage curves of the ZnO, and mixed ZnO:GaN(Ar) thin films grown in Ar gas ambient, under illumination with the UV/IR filter.

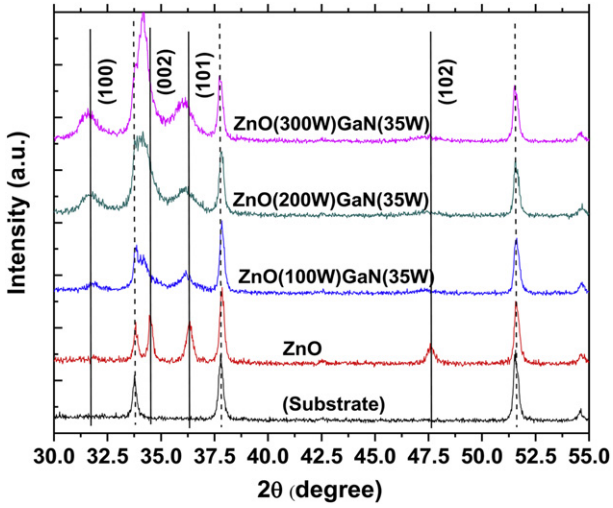

Fig. 4. X-ray diffraction curves of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient.

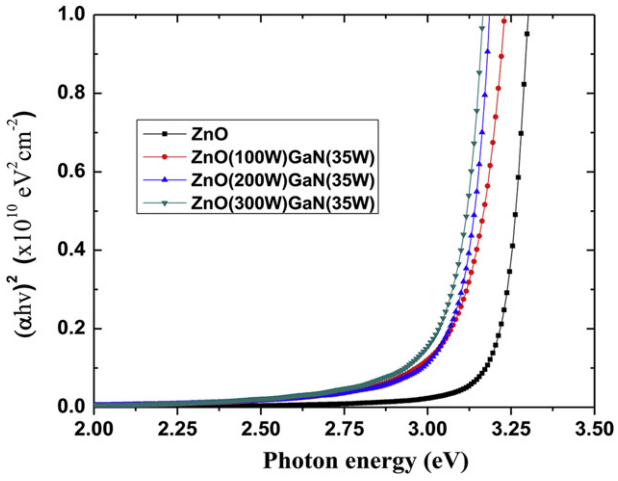

Fig. 5. The optical absorption coefficients of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient.

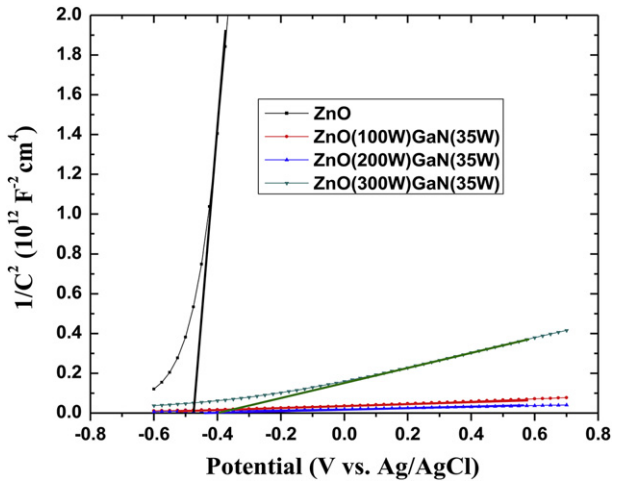

Fig. 6. The Mott–Schottky plots of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient.

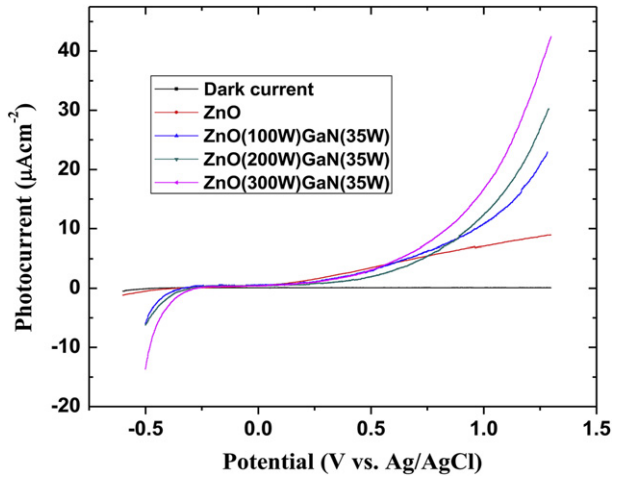

Fig. 7. The photocurrent–voltage curves of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient, under illumination with the UV/IR filter.

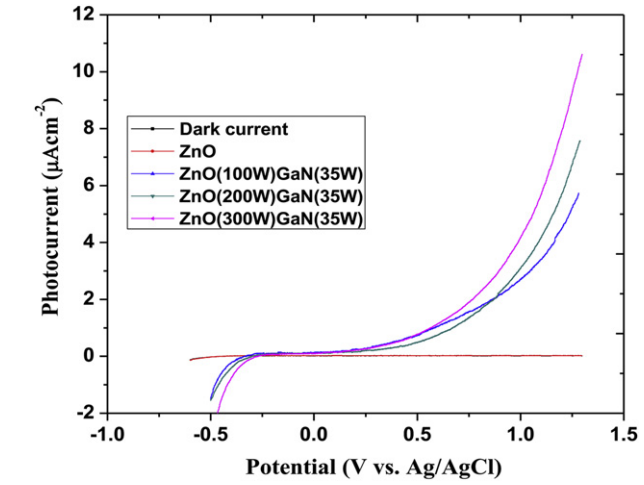

Fig. 8. Photocurrent–voltage curves of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient, under the illumination with the combined green and UV/IR filters.

narrowing of bandgap [26]. The absorption from this impurity band cannot be characterized by direct band transitions and typically results in an absorption tail in the measured optical absorption curve. Such an absorption tail is clearly evident in Fig. 5 for the mixed ZnO:GaN(N_2/O_2) thin films. This tail can be considered further bandgap reduction, which enables light harvesting in the much longer wavelength regions compared to the ZnO film. The Mott–Schottky plots of the ZnO and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient with N_2 mass flow rate of 75% are shown in Fig. 6. All the samples exhibited positive slopes, indicating n-type semiconductors. Our previous studies [13,14,20–22,29–31] reported that ZnO:N films deposited under a O_2/N_2 plasma showed the n-type behaviors, due to substitutional N_2 molecules which act as shallow double-donors. Perkins et al. [32] reported recently that O_2/N_2 plasma can contain significant fraction of N_2 molecules that can become incorporated into the ZnO films, leading to the n-type behavior.

The photocurrent–voltage curves of the ZnO, and mixed ZnO:GaN(N_2/O_2) thin films grown in mixed N_2 and O_2 gas ambient with N_2 mass flow rate of 75%, under illumination with the UV/IR filter is shown in Fig. 7. It showed clearly that the mixed ZnO:GaN(N_2/O_2) thin films exhibited enhanced photocurrents, compared to the ZnO film. The enhanced photocurrent may be due to the increased crystallinity, and bandgap reduction. At the potential of 1.2 V, the photocurrents were 7, 15, 18, and 32 μA cm^{-2} for the ZnO, 100 W, 200 W, and 300 W RF power of ZnO target for mixed ZnO:GaN(N_2/O_2) thin films, respectively. To investigate the photoresponse in the long-wavelength region, a green color filter was used in combination with the UV/IR filter as shown in Fig. 8. It is clear that the ZnO film showed no clear photoresponse, due to its wide bandgap. The mixed ZnO:GaN(N_2/O_2) films showed a photocurrent, in spite of much less light absorption. The results demonstrate clearly that significantly reduced bandgap with enhanced photocurrents can be obtained in (ZnO:GaN) films with mixed N_2 and O_2 gas ambient with varying the RF power approach.

4. Conclusions

The mixed (ZnO:GaN) thin films are synthesized by RF magnetron sputtering in Ar and mixed N_2 and O_2 gas ambient at 100 °C, followed by post-annealing in ammonia gas. The ZnO:GaN(Ar) films deposited under Ar gas ambient failed to narrow the bandgap,

whereas ZnO:GaN(N_2/O_2) thin films grown under mixed N_2 and O_2 exhibited enhanced crystallinity, with reduced bandgap. As a result, mixed ZnO:GaN(N_2/O_2) thin films exhibited enhanced photocurrent compared to ZnO thin film. The narrowing of the bandgap in mixed ZnO:GaN(N_2/O_2) thin films is realized by using the mixed N_2 and O_2 gas ambient and varying the RF power. Our results suggest that by using mixed N_2 and O_2 gas ambient, and varying the RF power, bandgap reduced (ZnO:GaN) thin films can be fabricated, with enhanced crystallinity and improved PEC response for solar driven hydrogen production.

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